Temporal and Spatial Scales of Terrestrially-derived Particulate and Dissolved Material in the Penobscot River System: Quantifying Conserved and Non-conserved Optical Properties and Transformations within the Estuary

Andrew H. Barnard
WET Labs, Inc., 620 Applegate Street, P.O. Box 518, Philomath, OR 97370
phone: (541) 929-5650 fax: (541) 929-5277 email: andrew@wetlabs.com

Collin S. Roesler
Ira C. Darling Marine Center, University of Maine, 193 Clark's Cove Road, Walpole, ME 04573
phone: (207) 563-3146 fax: (207) 563-3119 email: Collin.Roesler@maine.edu

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LONG-TERM GOALS

Coastal waters represent the commingling of offshore marine and terrestrial surface source waters and therefore are naturally complex and variable. Our long term goal is to establish observational and modeling approaches to predict sources and scales of variability in the source waters, particularly those related to land use activities in upstream watersheds, from observations and measurements in the coastal waters.

OBJECTIVES

Hydrologic optics provides an approach to characterizing physical and biogeochemical processes in aquatic systems over a range of time and space scales. The linkage between observations of the inherent optical properties (IOPs; absorption, scattering and fluorescence) and the geophysical properties lie in the establishment of robust optical proxies and the quantification of the temporal and spatial scales over which these proxies remain conservative in their properties. Our objectives are to identify and quantify specific optical and chemical characteristics of the colored particulate and dissolved fractions originating in the Penobscot River system that are associated with defined land use activities (land use proxies), and to determine the scales of variability over which these proxies can be detected both temporally (i.e. seasonal and episodic events) and spatially (from the source into coastal waters).

APPROACH

Our approach combines high resolution temporal and spatial hydrographic and optical observations from moored, surface underway and profiling platforms with chemical characterization of the organic and inorganic, particulate and dissolved carbon and nitrogen pools that originate in the sub-watershed drainage basins of the Penobscot River System and flow through Penobscot Bay estuary into the coastal waters of the Gulf of Maine. Our approach is to (1) identify optical proxies for bigeochemical parameters, including quantifying the time and space scales of conservative behavior; (2) apply these

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proxies to high-resolution time and space optical observations to compute concentration and flux of riverborne material into the estuary and coastal systems; (3) compare models for conserved behavior with observations to identify zones and times of non-conserved behavior; (4) elucidate transformation processes at these locations/times; (5) quantify impacts of land use on the biogeochemical properties of the coastal ocean with the goal to predict responses to climate induced hydrologic forcing.

WORK COMPLETED

We have continued to conduct approximately monthly sampling of 18 stations within the Penobscot River Watershed. At each station discrete water samples are collected for chemical and optical analyses: particulate organic carbon and nitrogen (POC and PON), dissolved organic carbon and nitrogen (DOC and DON), dissolved inorganic nutrients (NO_3, PO_4, SiO_2), fluorometric chlorophyll and pheopigments, total suspended solids and volatile solids (TSS and %VS), particle concentration and size distribution (Sequoia LISST, Agrawal and Pottsmith 2000), spectrophotometric particulate and dissolved absorption, and for selected samples, 3-d excitation/emission fluorescence (Coble 1996; Mayer et al. 1999; McKnight et al. 2001; Baker 2001; 2002a; 2002b). Additionally at each station, a WET Labs triplet sensor (chlorophyll and CDOM fluorescence and 650 nm backscattering) is deployed to obtain an in situ observation for comparison with the chemical and optical properties of the discrete water samples.

We have continued our long-term monitoring program of optical properties within the Penobscot River using moored WET Labs triplet sensors. Over the past year we have collected time series of chlorophyll and CDOM fluorescence and backscattering at various sites in the Penobscot River, most notably in the lower Penobscot River near a USGS gage station (Eddington, ME). We also continue to maintain optical sensors on the Gulf of Maine Ocean Observing System (GoMOOS).

As a part of a NASA study examining the transport and transformation of carbon within the Penobscot Bay and surrounding coastal regions, we have been maintaining an inline sampling system on a commercial ship based in Penobscot Bay. Data collected include physical (temperature and salinity) and optical (F_{Chl}, F_{cDOM} and beam attenuation at 660 nm) measurements in the surface waters. This system has provided over 28 large scale transects in the lower Penobscot River and Bay and the Gulf of Maine, and continues to this date.

We have also been conducting field surveys of the lower Penobscot River and western Penobscot Bay in order to characterize the spatial distribution of the dissolved and particulate materials as they flow through the Penobscot River and into the Bay. To date we have conducted 6 intensive field surveys of the region. Over the past reporting period, we have conducted two surveys; 15-16 November 2007 and 23-25 June 2008, mapping the spatial distributions of optical and physical parameters (Figure 1). Both of these surveys focused on characterizing the key transition region (~5 - 25 PSU) in terms of the distributions and concentrations of dissolved and particulate materials.

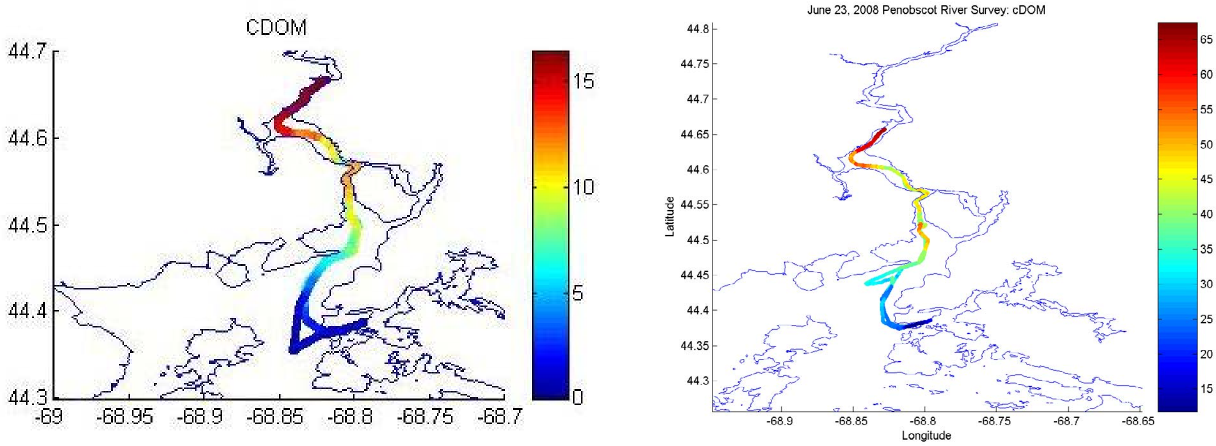

Figure 1. Spatial distributions of surface CDOM fluorescence within the upper Penobscot Bay region obtained during two separate field surveys using an inline sampling system installed on the RV Argo. Left panel shows the surface distributions of CDOM obtained on 15 November 2007. Right panel shows the surface distributions of CDOM obtained on 23 June 2008. Color bar shows the CDOM concentrations in units of ppb QSE for each panel.

The field surveys were conducted from the RV Argo Maine with our in line sampling system and which was augmented with a hyperspectral absorption/attenuation meter (AC-S) to provide addition spectral resolution in mapping the key optical parameters of the system. A profiling system equipped with spectral attenuation and absorption meters, backscattering sensors, chlorophyll and CDOM fluormeters, a CTD, and dissolved oxygen sensor was used to obtain the vertical distribution of dissolved and particulate materials along the salinity gradient through the lower Penobscot River and Bay. We also used a LISST to obtain vertical profiles of particle size distributions along this gradient. Water samples were collected for chlorophyll, spectral fluorescence and absorption, nutrients, particle size distributions, and dissolved organic carbon concentrations. During the June 2008 cruise, we also conducted a photobleaching experiment to characterize the dissolved organic transformations.

One of the major accomplishments over the past year was the procurement, configuration, and deployment of a turn-key surface water quality monitoring systems, termed the Land/Ocean Biogeochemcial Observatory (LOBO), in upper Penobscot Bay. This mooring is equipped with sensor packages for physical (temperature, conductivity, pressure, dissolved oxygen) and optical (F_{Chl} and F_{cDOM} and backscattering) and chemical (nitrate) properties in the upper 1 meter. While efforts conducted in the original funding were able to provide information as to the optical proxy temporal variability in the freshwater (river) and coastal endmembers (GoMOOS mooring F), we have not been able to fully resolve these time scales within the reactive region of the bay near 15 psu salinity. Thus, we installed the LOBO mooring system (Figure 2) to monitor the hourly variability in these parameters in order to understand how the optical proxies vary as a function of tides, episodic events, river runoff, and season. We also equipped this mooring with a particle size distribution sensor (LISST provided by CSR) to improve our understanding of the temporal variability in the particulate fraction. The LOBO system was deployed in the upper Penobscot Bay (Figure 2) on 22 June 2008, and has been providing continuous observations (every 2 hours) since deployment. The LOBO system was serviced for normal maintenance (battery replacement, cleaning, sensor calibration, etc) on August 23-25, 2008.

The LOBO system uses a cellular phone to transmit data (currently set to measure all parameters every 2 hours) to shore. A real-time data and information web site interface was also developed, and all data is publically available through this web site (http://penobscot.loboviz.com).

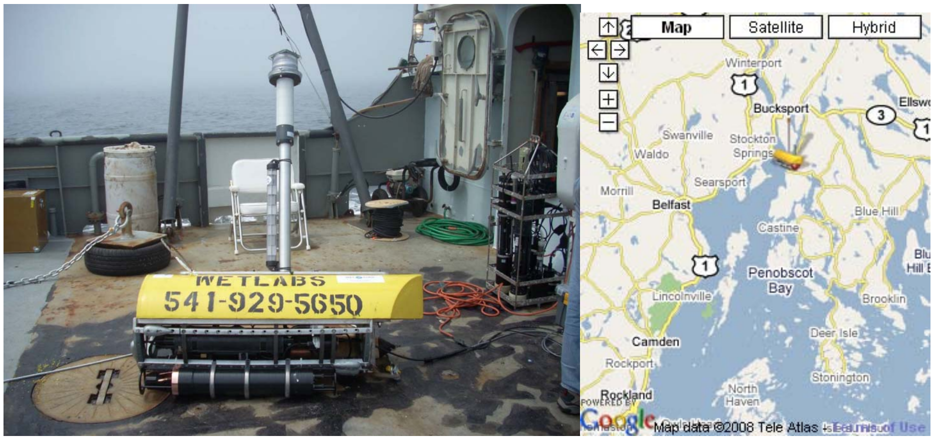

Figure 2. Left panel: Picture of the Penobscot Bay LOBO monitoring system on deck of the RV Argo ready to deploy. Sampling instrumentation, WET Labs WQM, FLCDS, Satlantic ISUS, and Sequoia LSST are mounted on the frame below the yellow floatation. Right panel: Map of the upper Penobscot Bay with the deployment location of the LOBO mooring shown as a yellow icon. The mooring is located south of the town of Bucksport, ME. Map courtesy of Google Earth.

RESULTS

Results of our observations to date have suggested that there are significant and traceable differences in the concentration and to a lesser extent the composition of materials entering the Penobscot River via tributary drainage basins and that this material undergoes transformations in the upper portion of Penobscot Bay. A major focus of our efforts has been to characterize the conservative/non-conservative behavior of these materials (dissolved and particulate) through the Penobscot estuary and bay. Our working hypothesis has been that during high flow periods, the material transport rate exceeds the transformation rate and that we can observe clear land use/coverage signals within Penobscot Bay and the coastal waters. However, during low flow periods, transformation exceeds transport and these signals may be degraded within the Bay.

To evaluate this hypothesis, we examined the spatial and temporal trends in our optical proxies using data collected from the inline system installed on the ship of opportunity. Eight transects covering the upper portion of Penobscot Bay and the lower Penobscot River were conducted in May, July, August, September and October 2006, and April, May, and November 2007. Most of these tracks extended north up river past the saltwater tidal range, and thus includes the freshwater endmember. Assuming a two endmember (freshwater and coastal oceanic water) mixing model applies to the Penobscot Bay, then properties which display a linear relationship with salinity across this transect are conserved (transport and mixing), while those that deviate from a simple linear relationship are not conserved (i.e transformed specific properties or exhibiting a source or sink within the system).

The optical property which shows the best correlation with salinity is cDOM fluorescence, regardless of sampling period. Our previous results have shown that F_{cDOM} is an excellent proxy for DOC concentration within the Penobscot River. Plotting the F_{cDOM} surface data from these 8 surface transects against salinity (Figure 3) demonstrates (1) how concentration is discharge dependent and (2) the non-conserved behavior within the estuary. In order to elucidate how much of the seasonal variability in the cDOM fluorescence is due to changes in the volume transport of the Penobscot River, we normalized the cDOM fluorescence data by the discharge measured at the USGS gage station at Eddington, ME for each sampling period. When normalized to discharge, the seasonal trend in cDOM delivery from the river entering into the bay show that the concentration is correlated with discharge (Figure 4). Several studies have shown strongly conservative (linear) relationships between dissolved absorption at 412nm and/or cDOM fluorescence and salinity for different freshwater inputs, indicating that this proxy can be used as a simple water mass tracer (Coble et al 1998; Twardowski and Donaghay 2001; Blough and Del Vecchio, 2002; Coble et al 2004). However, it is noteworthy that all sampling periods show pronounced non-conservative behavior, indicating that either transformations of the fluorescent DOC are occurring (i.e. that non-fluorescing matter from the river is being transformed to fluorescing matter) or that there is a source of new fluorescent cDOM within the estuary.

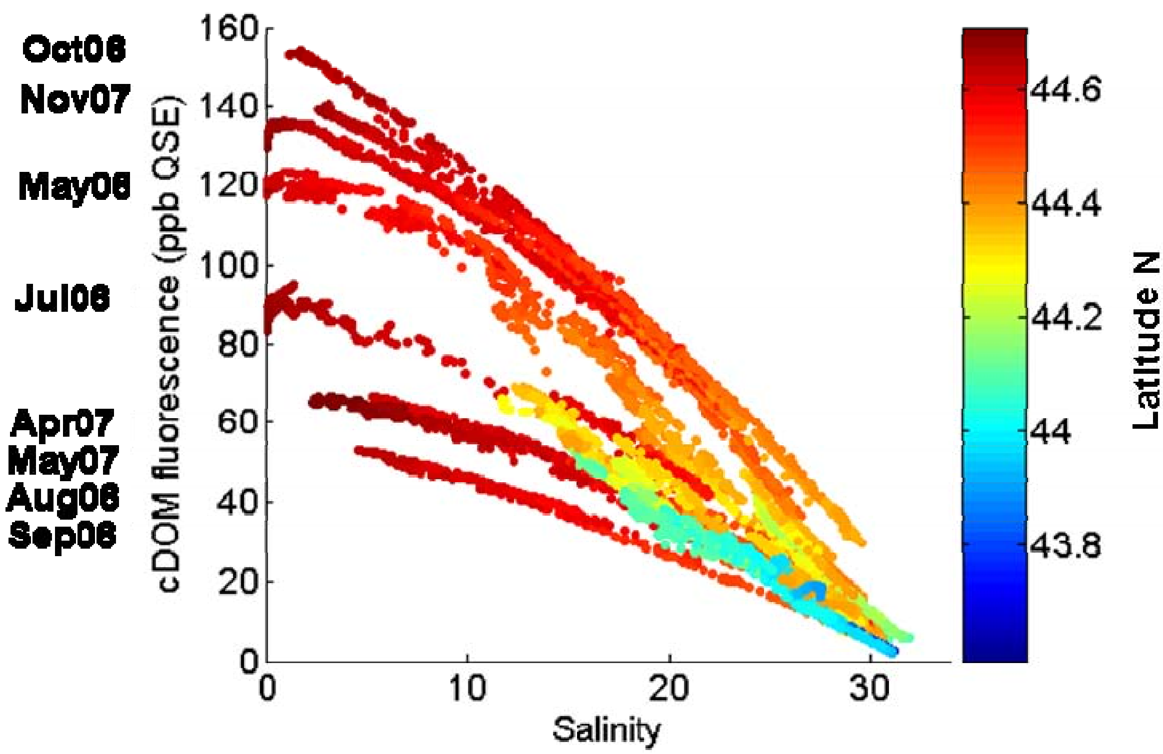

Figure 3. Surface distributions of salinity versus CDOM fluorescence throughout the lower Penobscot River and Penobscot Bay region obtained using an inline sampling system installed on the RV Argo. Data shown are from eight separate periods: May, July, August, September, and October 2006 and April, May, and November 2007. Colors indicate latitude where data was obtained (see colorbar). Shown to the left of the graph (at the maximum CDOM concentration at the lowest salinity) are the dates for each transect. Note that each of the eight transects shows a non-linear (non-conserved) behavior of CDOM with respect to salinity.

There appears to be a distinct change in slope at approximately 15 psu, indicating a source of fluorescent dissolved matter. However, when normalizing the cDOM delivery observations (F_{cdom} / discharge) by the cDOM delivery in at the low river station (F_{cdom} / discharge near the Eddington), the data collapses onto a single curve and the location of slope change is not a specific salinity value (which would imply a chemical process) but a specific geographic location (i.e. Frankfort Flats) suggesting that the transformation processes are likely physically mediated. Analysis of particle properties, from discrete and in situ observations, in this region show enhanced particle concentrations at all times of the year. It is uncertain if these particles are the result of tidal mixing and resuspension, chemical precipitation or aggregation. However, it is clear that this is a hot spot with respect to DOC transformation and that those transformations are likely to involve significant interaction with particulate matter.

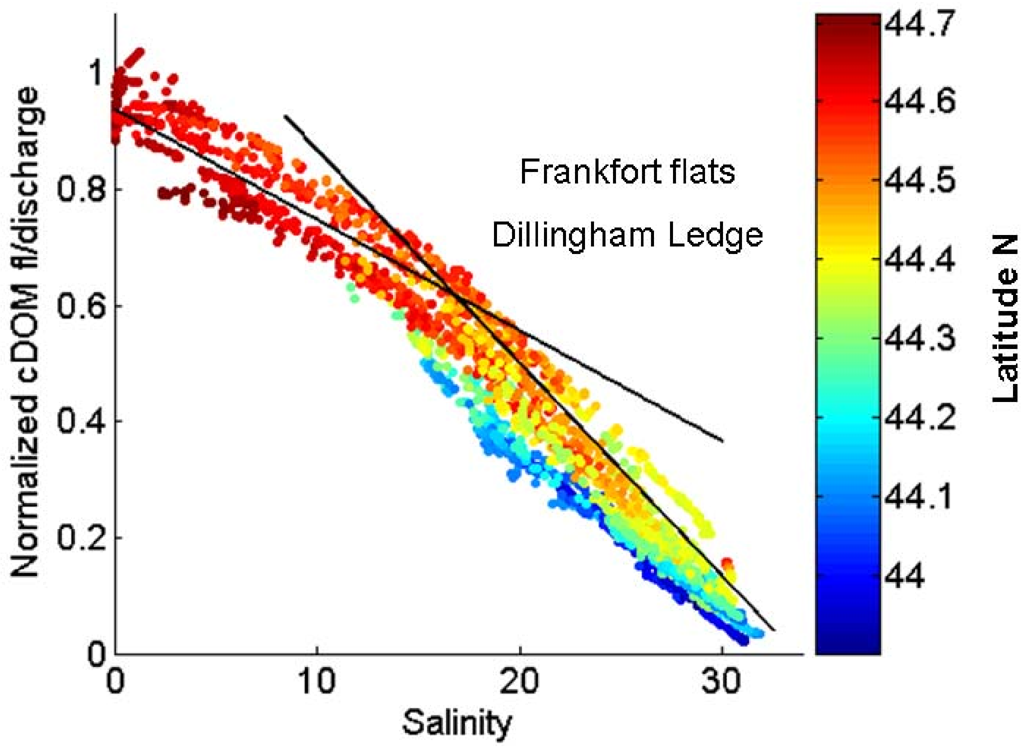

Figure 4. Surface distributions of salinity versus CDOM fluorescence normalized to the maximum and to the Penobscot river discharge (at Eddington, ME based on USGS data) throughout the lower Penobscot River and Penobscot Bay region. Data shown are from eight separate periods shown in Figure 3. Colors indicate latitude where data was obtained (see colorbar). Solid black lines indicate the two linear sections of the relationship. The intersection of these two lines typically occurs in the region near Bucksport, ME (from Frankfort Flats down to Stockton Springs, ME). The deployment location of the LOBO system (Figure 2) was selected to be within this transition area.

Based on the results above, significant transformations in the optical proxies, and thus the dissolved and particulate pools, appear to be occurring between our lowest sampling station (freshwater endmember) through the estuary to the salt water (oceanic) endmember. As was found for all cruises, the fluorescent dissolved matter appears to have a source in the region of Frankfort Flats, or there is an in situ transformation of nonfluorescent DOM to fluorescent DOM. This appears to be true for the chromophoric fraction of DOM (and hence DOC) as well. We also note that there is an apparent loss of fluorescent DOM at the mouth of the estuary in the waters 25 to 32 PSU, but no loss of chromophoric matter. However, the non-conserved behaviors are very different for the two optical pools as the F_{cDOM} to a_{g412} ratio is also non-conserved and indicates that there is a greater enhancement of the fluorescent DOM compared to the chromophoric DOM and this appears to be more tied to salinity compared to geographic location (i.e. chemically driven).

Every survey has demonstrated that the apparent site of non-conservative behavior in DOM is co-located with enhance particle concentrations, and that the transformation processes or input sources appear to be determined geographically and not at a certain salinity. This leads us to question the role of particulate matter in the transformation of the DOM, and to the driving mechanisms (river discharge, tides, nutrients, etc) that lead to these transformations. Our work to date as lead us to identify and quantify the magnitude, location, and timing of the non-conservative behavior in the particulate and dissolved organic matter and optical pools in the Penobscot River system. While we have discerned that the non-conservative behavior appears to be spatially and temporally coherent, we have not be able to identify the exact processes responsible for the non-conserved behavior or resolve the direct linkages between the particular and dissolved pools. The two specific questions we are seeking to address are 1) what are the controlling mechanisms for the DOC proxy changes (particle/bacterial/chemical mediation), and 2) what is the temporal variability in these transformations (changes with season, tidal mixing, DOC composition and delivery).

To assist in addressing these questions, we deployed aLOBO mooring on 22 June 2008 to monitor the temporal variability in surface distributions of temperature, salinity, dissolved oxygen, chlorophyll, CDOM, particles, and nitrate concentrations. All data from the LOBO system are freely available on the web (Figure 5) along with information describing the project and the instrumentation used (http://penobscot.loboviz.com). Observations from this mooring have highlighted the dual importance of the tidal fluctuations and the river discharge in the distributions of the dissolved and particulate materials (Figure 6). Over the next year, we expect to maintain this mooring, to provide a continuous time series of biogeochemical observations that can be used to examine the temporal scales of variability and importance of each parameter in driving the dissolved and particulate transformations.

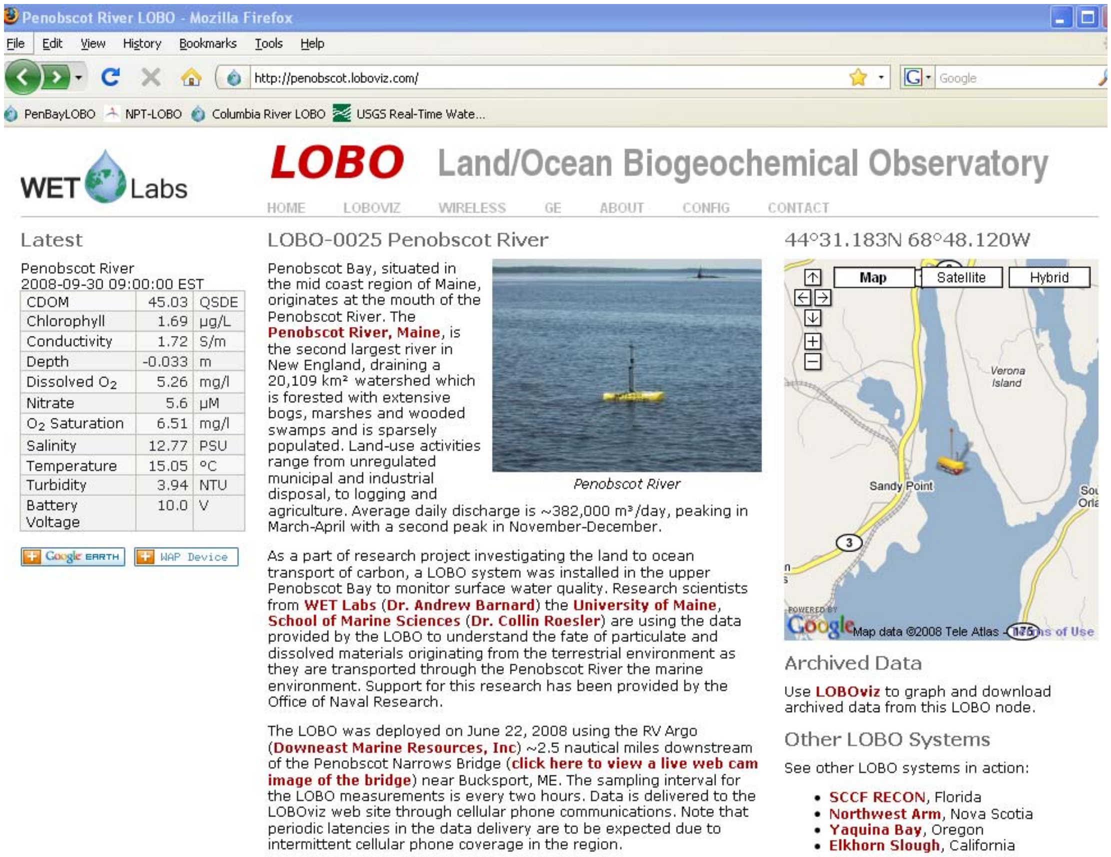

Figure 5. Penobscot Bay LOBO information web site home page. All data from the mooring is freely available through this site (http://penobscot.loboviz.com).

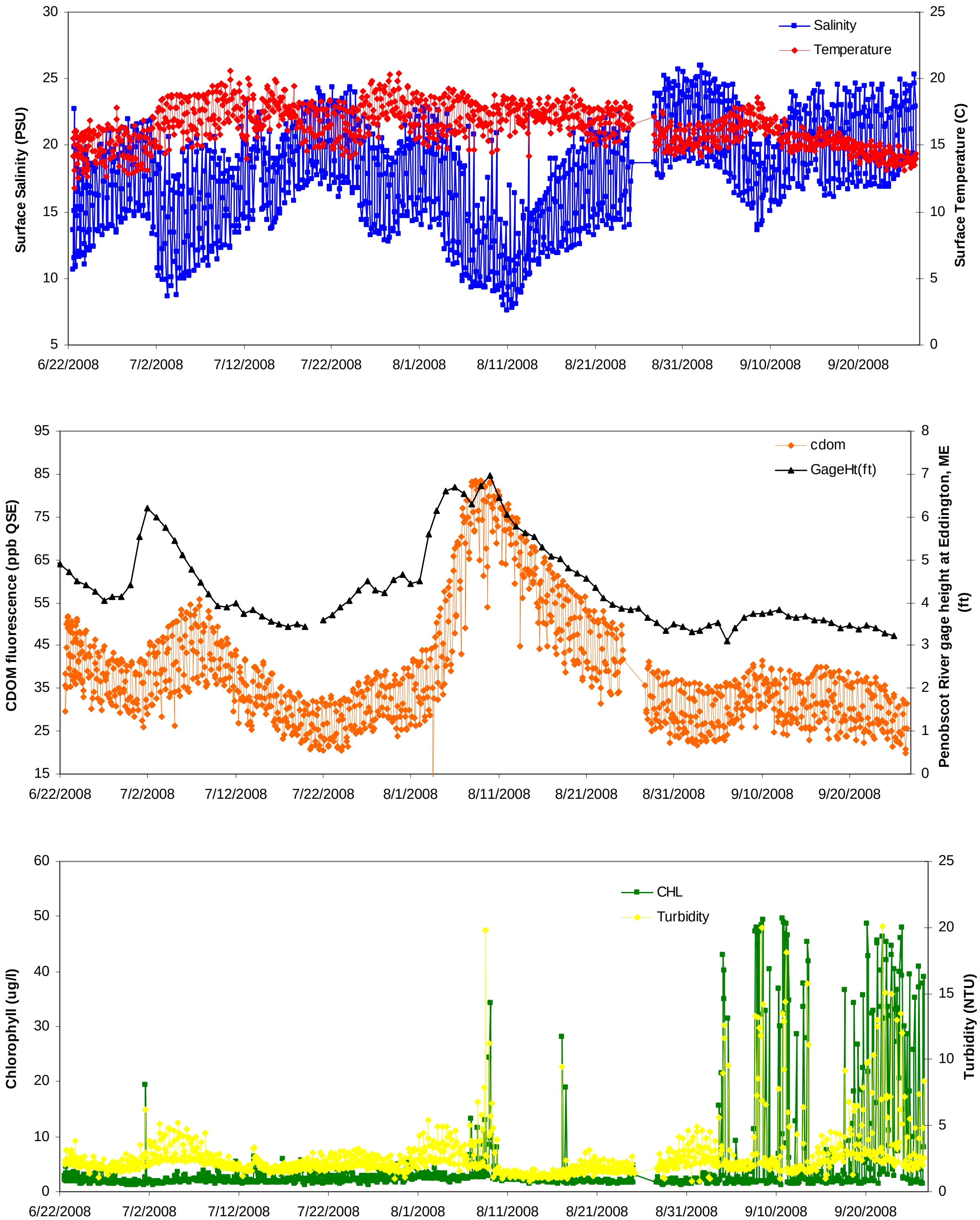

Figure 6. Surface data from 22 June through 25 September 2008 from the LOBO mooring installed in the upper Penobscot Bay region. Top panel shows the surface temperature and salinity, middle panel shows the CDOM fluorescence and river gage height (data courtesy of USGS) at Eddington, ME, bottom panel shows the surface chlorophyll fluorescence and turbidity. Note the strong tidal periodicity in salinity and the influence of the river discharge in the CDOM data.

IMPACT/APPLICATIONS

The results of this study will contribute to identification of optical and biogeochemical signatures associated with specific land use activities, and quantification of the tracer potential of those signatures through the river and estuarine system to the coastal environment. The application of this approach is the capability for determining changes in terrestrial land use from autonomous observations in the river and coastal waters. Identifying the conservative and nonconservative optical and chemical variability in the dissolved and particulate fractions of river inputs will also contribute to the development of coastal and watershed models of carbon flux. The high temporal resolution data obtained in this study will allow for quantification of this variability on time scales of hours to months, covering a range of scales from daily to seasonal to interannual and including and episodic events. While the focus of this study does not address the specific transformations operating within a riverine impacted regions, these results will be useful in aiding our understanding of the relevant biogeochemical processes operating in the coastal margins influenced by riverine inputs by determining the appropriate temporal and spatial scales of optical and chemical variability that are conserved though the system.

TRANSITIONS

The USGS Augusta, ME office has shown a strong interest in transitioning the ECO triplet river observation systems we will be deploying in the Penobscot River. We have worked with the USGS to implement using these sensors as part of their field sampling program within the Penobscot River and its tributaries. The LOBO mooring deployed in upper Penobscot Bay through this project is providing real-time bio-optical and physical data, and all data is available through the LOBO web interface (http://penobscot.loboviz.com). Over the next year, we will work to integrate these data into regional ocean observing data systems (i.e. GoMOOS, NERACOOS), as well as promote and promulgate the use of these data by state and federal agencies. We are also tracking the web site traffic and data downloads to understand the utility of these data outside of the research community.

RELATED PROJECTS

1. Both C. Roesler and A. Barnard are Co-PIs on a NASA sponsored multi-investigator research project examining the variability in fluxes of dissolved and particulate organic carbon from terrestrial sources to the Gulf of Maine via major rivers, and their subsequent fate within the Gulf of Maine. This work is specifically focusing on the impacts of riverine dissolved and particulate loading to the carbon cycle of coastal and offshore systems. Our ONR project is highly complementary to this project, as it is providing a better understanding of the variability in the concentration and composition of the Penobscot River dissolved and particulate materials and its subsequent delivery to the coastal and offshore regions.

2. The Gulf of Maine Ocean Observing System (GoMOOS), which Dr. Roesler is funded by to maintain optical instrumentation and data streams from the mooring observation program, is providing valuable hourly time series of coastal optical and physical surface properties upstream and downstream of the Penobscot River. Beginning in the fall of 2004, optical sensors (backscattering, chlorophyll and cDOM fluorometers) were installed on a GoMOOS mooring in the center of the mouth of the western branch of Penobscot Bay. Data from these systems are providing a wealth of information as to the hourly to seasonal variability in the

dissolved and particulate materials within the river to coastal transition zone of the Penobscot Bay.

3. Dr. Barnard is involved with the Coastal Margin Observation and Prediction (CMOP) Science and Technology Center (Oregon Health and Sciences University, NSF) to develop, deploy, and maintain a Land/Ocean Biogeochemical Observatory (LOBO) node for the lower Columbia River. Similar to the LOBO system used in the Penobscot, the Columbia River node includes the same sensing suite (http://columbia.loboviz.com). The goals of this project are to understand the role of large sediment fluxes on the dissolve organic materials. This mooring will also integrate an in situ phosphate sensor over the next year to more fully characterize the nutrient variability within the lower Columbia River.

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